OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-96-1-0088

PR Number: 96PR01257-00

Synthesis of Polymeric Families with Highly Delocalized Electronic States for Electronic and Photonic Applications

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 96PR01257-00
Contract/Grant Number: N00014-96-1-0088
Contract/Grant Title: Synthesis of Polymeric Families with Highly Delocalized Electronic States for Electronic and Photonic Applications
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a. Number of papers submitted to refereed journals, but not published: 3
b. + Number of papers published in refereed journals (for each, provide a complete citation): 6
c. + Number of books or chapters submitted, but not yet published: 0
d. + Number of books or chapters published (for each, provide a complete citation): 0
e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 1
f. Number of patents filed: 0
g. + Number of patents granted (for each, provide a complete citation): 1
h. + Number of invited presentations (for each, provide a complete citation): 16
i. + Number of submitted presentations (for each, provide a complete citation): 0
j. + Honors/Awards/Prizes for contract/grant employees (list attached): 3
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:
Graduate Students: 2.5
Post-Doctoral Associates: 0.5
including the number of,
Female Graduate Students: 1.0
Female Post-Doctoral Associates: 0
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0.3 (Hispanic)
Asian Graduate Students: 1.6
Asian Post-Doctoral Associates: 0
l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

+ Use the letter and an appropriate title as a heading for your list, e.g.: b. Published Papers in Refereed Journals, or, d. Books and Chapters published.
* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

PART I

a. Papers submitted to refereed journals (and not yet published):

1. Yao, Y.; Zhang, Q. T.; Tour, J. M. "Synthesis of Imine-Bridged Planar Poly(pyridinethiophene)s. Combination of Planarization and Intramolecular Charge Transfer in Conjugated Polymers," *Macromolecules*, under review.
2. Morgan, A. B.; Tour, J. M. "Synthesis and Testing of Non-Halogenated Alkyne/Phosphorus-Containing Polymer Additives. Potent Condensed Phase Flame Retardants," *J. Appl. Polym. Sci.*, under review.
3. Cassell, A. M.; Scrivens, W. A.; Tour, J. M. "DNA/Fullerene Hybrid Materials," *Angew. Chem.*, in press.

b. Papers published in refereed journals:

1. Zhang, Q.; Tour, J. M. "Alternating Donor/Acceptor Repeat Units in Polythiophenes. Intramolecular Charge Transfer for Reducing the Bandgaps in Fully Substituted Conjugated Polymers," *J. Am. Chem. Soc.* **1998**, *120*, 5355-5362.
2. Morgan, A. B.; Tour, J. M. "Synthesis and Testing of Nonhalogenated Alkyne-Containing Flame-Retarding Polymer Additives," *Macromolecules* **1998**, *31*, 2857-2865.
3. Choi, D.-S.; Huang, S.; Huang, M.; Barnard, T. S.; Adams, R. D.; Seminario, J. M.; Tour, J. M. "Revised Structures of *N*-Substituted Dibrominated Pyrrole Derivatives and Their Polymeric Products. Termaleimide Models With Low Optical Bandgaps," *J. Org. Chem.* **1998**, *63*, 2646-2655.
4. Yao, Y.; Lamba, J. J. S., Tour, J. M. "Synthesis of Highly Functionalized Pyridines for Planar Polymers. Maximized _-Conjugation in Electron Deficient Macromolecules," *J. Am. Chem. Soc.* **1998**, *120*, 2805-2810.
5. John, J. A.; Tour, J. M. "Synthesis of Polyphenylene Derivatives by Thermolysis of Enediynes and Dialkynylaromatic Monomers," *Tetrahedron* **1997**, *53*, 15515-15534.
6. Zhang, Q. T.; Tour, J. M. "Imine-Bridged Planar Poly(phenylene-thiophene)s and Polythiophenes," *J. Am. Chem. Soc.* **1997**, *119*, 9624-9631.

c. Books or chapters submitted, but not yet published: None.

d. Books or chapters published: None.

e. Technical Reports Published and Papers Published in Non-Refereed Journals:

Yao, Y.; Lamba, J. J. S., Tour, J. M. "Synthesis of Imine-Bridged Planar Polypyridines," *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*(1), 290-291.

f. Patents Filed: None

g. Patents Granted:

Tour, J. M.; Scrivens, W. A.; Bedworth, P. V. "Purification of Fullerenes," U.S. Patent 5,662,876, September 2, 1997.

h. Invited Presentations:

1. Conjugated Oligomers and Polymers for Electronic and Photonic Applications, Syracuse University, Department of Molecular Electronics, Syracuse NY, June 11, 1997.
1. Defense Advanced Research Projects Agency, Review, Harvard University, Cambridge MA, June 29, 1997.
2. Conjugated Oligomers and Polymers for Electronic and Photonic Applications, Cambridge Healthtech Assoc., Nanoscale Systems Conference, San Francisco CA, June 27, 1997.
3. Defense Advanced Research Projects Agency, Review, Santa Fe NM, October 29, 1997.
4. Conjugated Oligomers and Polymers for Electronic and Photonic Applications, Foresight Conference on Nanotechnology, Palo Alto CA, November 7, 1997.
5. Conjugated Oligomers and Polymers for Electronic and Photonic Applications, University of Wisconsin, Department of Chemistry, Madison WI, December 11, 1997.
6. Molecular Electronics, Engineering Foundation, Puerto Rico, December 16, 1997.
7. MITRE-based Conference on Molecular Electronics sponsored by the Defense Advanced Research Projects Agency, McLean, VA, February 2, 1998.
8. Selected Research Topics and the Passion of Science, University of South Carolina, Joint Board Retreat, Charleston SC, February 20, 1998.
9. Conjugated Oligomers and Polymers for Electronic and Photonic Applications, University of Akron, Department of Chemistry, Akron OH, March 11, 1998.
10. Defense Advanced Research Projects Agency, GOMAC Meeting, Washington DC, March 19, 1998.
11. Conjugated Oligomers and Polymers for Electronic and Photonic Applications, American Chemical Society, National Meeting, Division of Polymer Chemistry, Dallas Texas, March 30, 1998.
12. Conjugated Oligomers and Polymers for Electronic and Photonic Applications, Rice University, Department of Chemistry, Houston TX, April 17, 1998.
13. Conjugated Oligomers and Polymers for Electronic and Photonic Applications, IBM Corporation, T. J. Watson Research Center, Tarrytown NY, April 29, 1998.
14. Conjugated Oligomers and Polymers for Electronic and Photonic Applications, Department of Chemistry, Indian Institute of Chemical Technology and Osmania University, Hyderabad India, May 27, 1998.
15. Department of Chemistry, University of Hyderabad, Hyderabad India, May 28, 1998.
16. Conjugated Oligomers and Polymers for Electronic, Photonic, and Flame Retardant Polymer Additive Applications, Office of Naval Research, Program Review, Jacksonville, FL, June 2, 1998.

i. Submitted Presentations: None.

j. Honors/Awards/Prizes:

1. National Defense Science Study Group, Based out of the Institute for Defense Analysis, January 1998-present.
2. Governor's Mathematics and Science Advisory Board for South Carolina, September 1996 to present.
3. Guy F. Lipscomb Professor of Chemistry, University of South Carolina, Columbia, SC, August 1996 to present.

I. Other Funding:

Active Support:

1. Defense Advanced Research Projects Agency, subcontract from Yale University (Professor Mark Reed): *Self-Assembly Based Approaches to Microelectronics Fabrication and Devices: Surface Passivation, Soft Lithography, Electrically Functional Systems, and Hierarchical Self-Assembly,* Period 6/1/95 - 5/31/98. Total direct three year support is $588,000 to J. Tour's group. The proposal is a joint effort with Yale University (M. Reed), Pennsylvania State University (D. Allara), Harvard University (G. Whitesides) and Motorola Corporation (H. Goronkin and G. Maracas). This will continue our work on to synthesize conjugated organic oligomers of known length with end group control to make wires, transistors, and circuits based on single molecules. We will work with the Yale Microelectronics Center for incorporation of these molecules into nanolithographic assemblies. There is no direct overlap with between the DARPA and this ONR grant. Some of the systems synthesized with DARPA funds are being screened for NLO and LED activity using ONR funds.
2. Federal Aviation Administration, "Synthesis and Characterization of New Flame Resistant Materials", written with M. Angel, 9/1/95- 8/31/98, $175,300 for J. Tour. The FAA funds one student plus some equipment. Supplement to ONR funds, therefore, leveraging achieved.
3. Department of Energy, EPSCoR, "Electrochemical Cells based on Fullerene Nanotubes", 10/15/95-10/14/97, $152,000 for J. Tour. This grant idea was initially started with ONR and NSF PYI funds. The ONR grant supports the work on nanotube composites, to a small extent.
4. National Science Foundation, Synthesis of Precise Unnatural Oligomers Using Well-Defined Synthetic and DNA Templates", 7/1/96-6/30/97, $50,000. PI, F146. No overlap with this ONR grant.
5. National Science Foundation/EPSCoR, "Fundamental Studies at Polymer/Materials Interfaces: A Junior Faculty Development Proposal in Optical Sensing", 9/1/96-8/81/99, $950,000, co-PI with several faculty, acting as the faculty mentor, ~$15,000 in summer salary to J. Tour. Some of the systems prepared the ONR grant will be screened by this collaborative effort.
6. Albemarle Corporation, "Alkyne Based Flame Retardants: A New Class of Non-Halogenated Flame Retardants for Polymers," 9/15/97-9/14/98, $64,243, PI. Supplement to ONR funds, therefore, leveraging achieved.
7. NSF, "Purchase of a SQUID Magnetometer" $85,700, 01/01/97-12/31/97, co-PI.
8. Office of Naval Research, "University Research Initiative Program for Combat Readiness" [19 projects: PI on one ("Molecular Scale Electronic Arrays for the Design of Ultra-Dense and Ultra-Fast Computational Systems," with J. Seminario and M. L. Myrick); Co-PI on one ("Accelerated Research in Biofouling Control," with M. M. Fletcher, C. R. Lovell, P. A. Noble, and A. W. Decho) $9.3 million, 1997-2000. No overlap with this ONR work.
9. NSF, "Upgrade of Data System for Mass Spectrometer," $70,744, 7/1/97-6/30/98, co-PI.
10. NASA, "Computational Studies to Direct Syntheses and Correlate Electronic Property Data on Molecular Scale Wires, Interconnects, and Devices," supercomputer time only, PI. No overlap with this ONR work.
11. NASA-Goddard Space Center, "Computational Studies to Direct Syntheses and Correlate Electronic Property Data on Molecular Scale Wires, Interconnects, and Devices," supercomputer time only, co-PI. No overlap with this ONR work.

PART II

a. Principal Investigator: James M. Tour

b. Phone: (803) 777-9517

c. Cognizant ONR Scientific Officers: Drs. Kenneth J. Wynne and Angel Ervin.

d. Program Objective:

New synthetic organometallic reactions can be used to synthesize novel, well-defined conjugated polymer systems for interesting electronic, photonic, and high performance (flame retarding) materials applications.

e. Significant Results during the last year:

1. Control of bandgap modulation is at the heart of several new device technologies including nonlinear optics, light emitting diodes, photovoltaic devices, polymer-based laser components, optoelectric sensors. Two entirely new classes of compounds were made available for optoelectronic screening which include planar conjugated polymers and donor/acceptor-type polymers for bandgap control.
2. A route was developed to donor/acceptor/buffer polymers for the maximization of the dipole moment in rigid rod polymers.
3. Development of a molecular tripling strategy for controlled oligomer synthesis.
4. We have developed a method for template oligomerization for controlled oligomer synthesis. DNA can be used as a scaffold for the synthesis of controlled materials up to microns in size, but with 300 Å diameters, thus yielding a new route to well controlled materials synthesis. DNA is not the only template being investigated.
5. We have developed several new high char yielding non-halogenated polymer additives. We have secured funding through the Federal Aviation Administration (one student plus equipment) and Albemarle Corporation (one post doc) to further investigate these compounds. Albemarle Corp. will purchase patent rights to a new halogen-free compound that provides V=0 flame retardancy to polycarbonate and excellent flame inhibition properties to the commodity plastic ABS. This could have enormous monetary impact.

f. Brief summary of plans for next year:

1. Working with AAI ABTECH Corporation on the development of an "electronic nose" and trauma state evaluation breathalyzer based on our novel conjugated materials.
2. We will team up with optoelectronics specialists for the further evaluation of our novel conjugated materials.
3. A more soluble version of our donor/acceptor/buffer polymers will be prepared.
4. We will delineate the scope of template oligomerization.
5. We will continue to explore the efficacy of condensed phase flame retardants.

g. Graduate students and postdocs presently working on the ONR Projects: D. Brian Shortell, Alex Morgan, G. Miracle and A. Devasagayarai.

PART III:

See the PowerPoint-98 presentation.

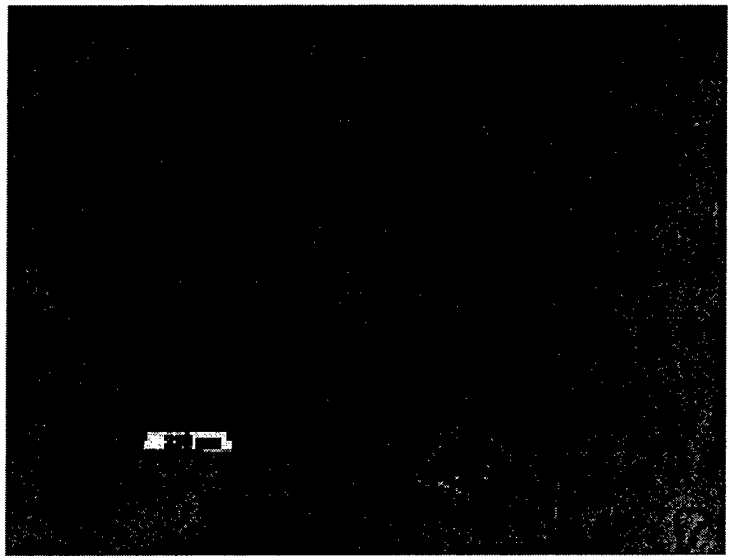
Synthesis of Polymers with Delocalized Electronic States for Electronic, Photonic, and High Performance Materials Applications

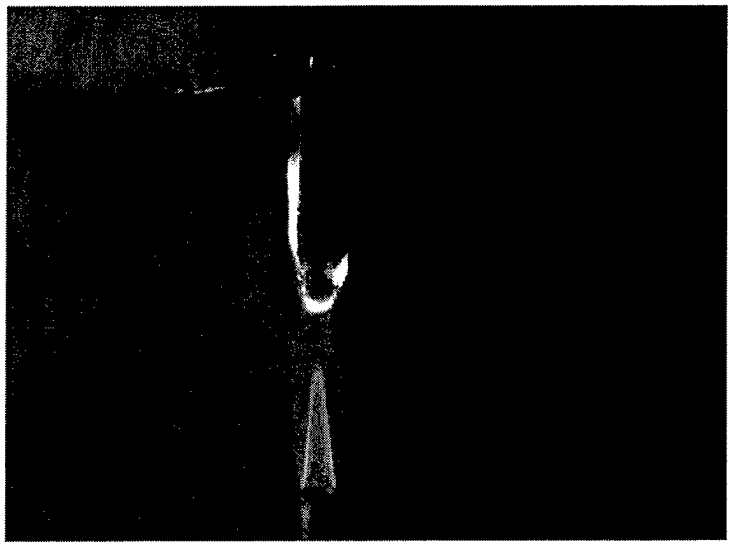
James M. Tour, University of South Carolina

Objectives: Develop rapid routes to precisely defined materials for electronic, photonic, and high performance materials applications.

Approach: (1) Use templates to provide access to materials of precise size and constitution in a single step.
(2) Use non-halogenated and non-toxic condensed-phase flame retardants as substitutes for commercial brominated polymer additives in plastics.

Accomplishments: (1) Synthesized nanometer-sized rings of conjugated materials in a single step (Fig 1, 250 nm scale bar).
(2) One-pot synthesis of a non-toxic, white, non-halogenated flame retardant for ABS and polycarbonate (Fig 2, notice char).





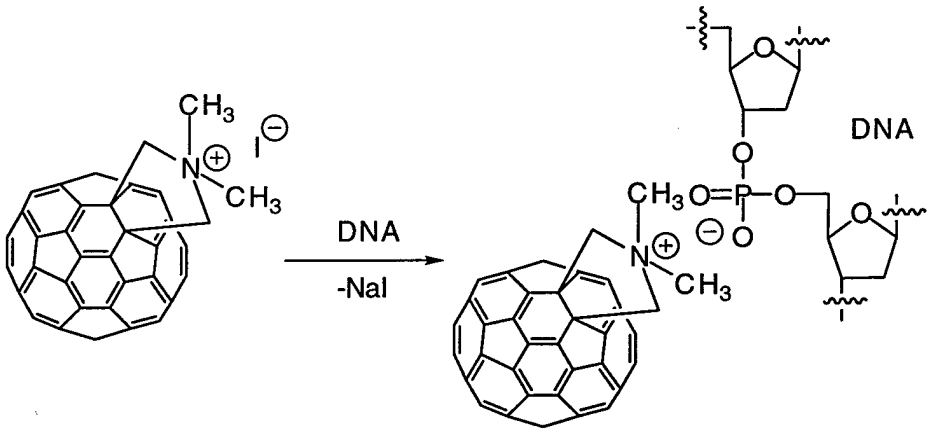
Impact & Transition:

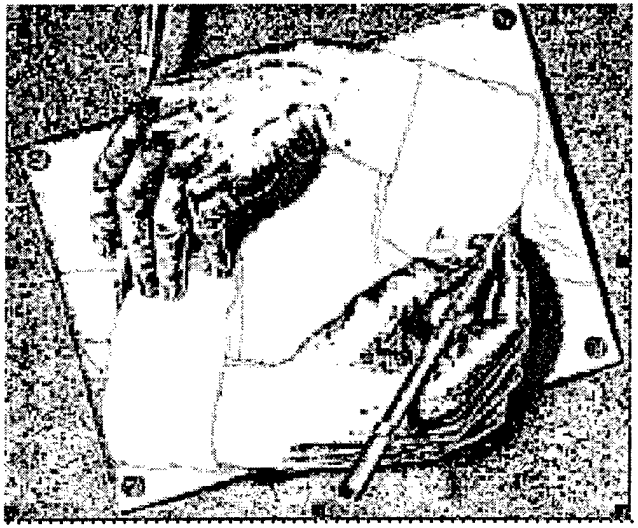
(1) Rapid template synthesis method can provide a route to precisely defined (length and constitution) materials ranging from the nanometer to centimeter size regimes to impact technologies ranging from electrooptics to catalysis.
(2) The new flame retardants are being patented by Albemarle Corporation. This could have a very large economic and environmental impact on future generations of commercial flame retardant additives.

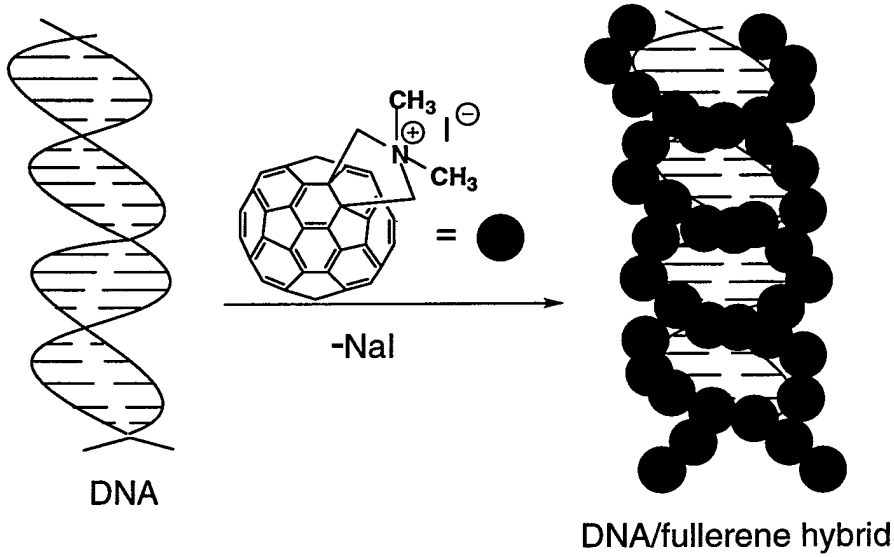
Template Synthesis of Precisely Defined Materials

James M. Tour, University of South Carolina

The ultimate goal of polymerization reactions is the precise control of macromolecular length, constitution, stereochemistry, and sequence. Nature accomplishes this through template directed syntheses. Using DNA as a template for materials of precise length, C60 was complexed through a simple ion exchange to afford conjugated nanometer-sized rings.

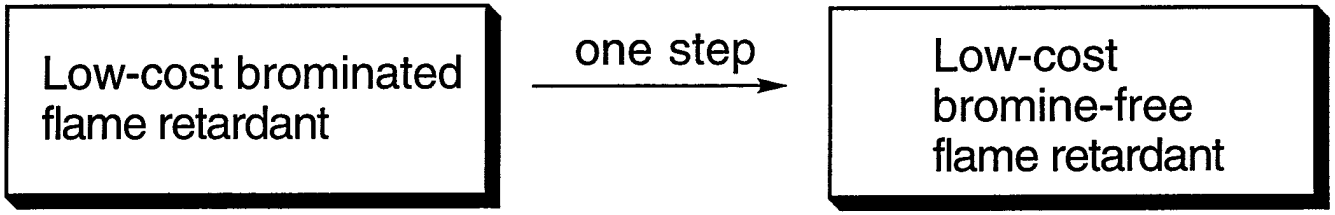






Flame Retarding Polymer Additives

James M. Tour, University of South Carolina



The newly developed compound* is non-toxic, white, non-phosphorous-containing and not easily photochemically degrade.

At 5 wt % addition to polycarbonate, a V_0 is obtained (<10 sec self-extinguishing with no dripping).

At 10 wt % addition to ABS, a 5-6 minute burn (very slow) ensues with no dripping. This fulfills several standard European burn retardation requirements. A synergist screening is being done to develop self-extinguishing combinations.

*Albemarle Corporation is paying patent costs.

Explanatory Text for Viewgraphs 1-3

James M. Tour, University of South Carolina

Viewgraph 1

• Shown at the top right is a TEM picture of plasmid (circular) DNA (ϕX174 RFII, a popular electron microscopy standard, pre-relaxed plasmid, 5386 bp, 10 μg/mL, 10 mM Tris-HCl, pH 8.5) that is imaged without heavy metal staining. The fullerenes disperse the electron density sufficiently to achieve imaging without the need for stains. Hence, the ringed DNAs are heavily sheathed in fullerenes.

• Bottom right showns the actual burn test with a calibrated methane/air flame applied directly to polycarbonate that contains 5 wt % of the newly developed non-halogenated polymer additive. Notice the heavy char that forms since these are condensed phase flame retardants. Removal of the flame will result in flame extinguishing without polymer dripping.

Viewgraph 2, The method of template directed oligomer synthesis is being explored from several avenues. The one shown used DNA as a template for the synthesis of conjugated nanomaterials. Whatever the size and shape that the DNA possesses, in a simple one-pot operation, the shape can be duplicated to afford conjugated monolithic or networked structures. Efforts are underway to assess the conductivity of these naonomaterials.

Viewgraph 3. The newly developed compound (proprietary until patent application is filed by Albemarle Corporation- ONR patent office has been notified of the disclosure) is non-toxic, white, contains no phosphorous, is not photochemically degraded, and can be prepared in one-pot from commercial brominated flame retardants. The Underwriter's Laboratory industrial standard flame test (UL-94) is passed with polycarbonate with 5 wt % addition of the additive. The burn times on ABS are greatly prolonged to 5 minutes, thereby suggesting great potential as a condensed phase retardant even for commodity plastics.